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(54) **A lead-free tin-silver-based soldering alloy**

(57) The present invention provides a lead-free tin-silver-based soldering alloy which has a low melting point equal to an alloy H without containing harmful lead, expensive In or the like, and is excellent in mechanical characteristic, that is, a tensile strength, an elongation value and heat fatigue characteristic as compared with

the alloy H, and thus, is applicable to a soldering work at a low temperature and can make high reliability and long useful life or durable year of products. The lead-free tin-silver-based soldering alloy consists essentially of Ag: 2 to 4% by weight, Zn: 0.5 to 2% by weight, Bi: 2 to 6% by weight, and a balance being substantially Sn.

EP 0 882 544 A1

Description**BACKGROUND OF THE INVENTION**

a) Field of the Invention

The present invention relates to a lead-free tin-silver-based soldering alloy, and more particular, to a soldering alloy which has a low melting point equal substantially to an alloy H which is a general lead-free tin-silver-based soldering alloy, and is excellent in mechanical characteristic, that is, in a tensile strength, an elongation value and heat resistant fatigue characteristic.

b) Description of the Prior Art

Conventionally, lead has been contained in a soldering alloy. In recent years, the lead has been eluted from wasted IC chips, printed circuit boards or the like; as result, groundwater is contaminated. For this reason, there has arisen an environmental problem such as lead poisoning or the like. Under such circumstances, the study and development of a lead-free soldering alloy have been made, and then, various lead-free soldering alloys have been proposed. In general, an alloy H (manufactured of Nippon Alpha Metals Co., Ltd.) has been well known as a lead-free soldering alloy which is used in the aforesaid IC chips, printed circuit boards, etc. The alloy H consists essentially of Ag: 2.0% by weight, Cu: 0.5% by weight, Bi: 7.5% by weight and a balance being Sn. Further, the alloy H has a melting point of 212°C which is higher than a Pb-Sn eutectic solder, and has a melting point lower than a conventional silver-tin-based soldering alloy which does not contain Pb, Cd or the like, and is excellent in melting characteristic. However, in the alloy H, an elongation value is low in a tensile test, and there exists a low temperature eutectic phenomenon. Further, if the alloy H is kept at a high temperature, the elongation of the alloy H is deteriorated; for this reason, the alloy H has inferior heat fatigue characteristic. Further, the alloy H can not absorb a thermal expansion difference between the printed circuit board and components when a temperature cycle is applied to a soldering portion; for this reason, there is the possibility that what is called, the soldering portion is fractured.

Inventors of the present invention have made various studies in order to find a soldering alloy which does not contain harmful lead or the like in environmental hygiene, and is excellent in melting characteristic, a tensile strength and an elongation value. Further, inventors have previously proposed the invention (alloy) disclosed in Japanese Patent Application Laid-Open No. 187590 (1996) or in Japanese Patent Application Laid-Open No. 19892 (1996). However, the invention (alloy) disclosed in these Publications was inferior to the alloy H in the melting characteristic. Moreover, the aforesaid alloy contains a very expensive In; for this reason, it was difficult to say that the disclosed alloy is a desirable alloy.

SUMMARY OF THE INVENTION

The present invention has been made taking the aforesaid problem in the prior art into consideration. An object of the present invention is to provide a lead-free tin-silver-based soldering alloy which has a low melting point equal to an alloy H without containing harmful lead, expensive In or the like, and is excellent in mechanical characteristic, that is, a tensile strength, an elongation value and heat fatigue characteristic as compared with the alloy H, and thus, is applicable to a soldering work at a low temperature and can make high reliability and long useful life of products.

To achieve the above object, the present invention provides a lead-free tin-silver-based soldering alloy consisting essentially of Ag: 2 to 4% by weight, Zn: 0.5 to 2% by weight, Bi: 2 to 6% by weight, and a balance being substantially Sn.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The aforesaid alloy of the present invention is obtained by adding Zn and Bi to a tin-silver-based soldering alloy consisting of Sn-Ag. Ag has the effect of lowering a melting point, and further, increases a strength and makes brightness well. In order to obtain the aforesaid effect, Ag of 2% by weight or more need to be added. On the other hand, from the phase diagram of Sn-Ag, the following matters are evident. More specifically, the melting point of Ag becomes the lowest when Ag of 3.5% by weight is added. If Ag of 3.5% by weight or more is added, conversely, the melting point of Ag becomes high. As is evident from the above facts, even if Ag of 4% by weight or more is added, the cost merely becomes high, and there is no effect of lowering a melting point. Therefore, the upper limit of Ag additive amount is 4% by weight. Zn has the effect of lowering a melting point and improving a mechanical strength, and it is preferable that Zn of 0.5% by weight or more is added. However, if Zn is added too much, wettability is deteriorated; for this reason, Zn is set to 2% by weight or less. Bi of 2% by weight or more need to be added in order to obtain a low melting point equal to the alloy H. However, if Bi is added too much, elongation is lowered, and low temperature eutectic exists

therein; for this reason, the upper limit of Bi additive amount is 6% by weight.

By employing the composition within the range as described above, there can be provided a soldering alloy which has a melting point of low temperature equal to the alloy H, and is excellent in mechanical strength, that is, a tensile strength, elongation and mechanical characteristic after being kept at a high temperature. As a result, a soldering alloy, which is excellent in heat fatigue characteristic, can be obtained. Therefore, it is possible to obtain a soldering alloy which can perform a soldering work at a relatively low temperature, reduce the possibility of damaging a printed circuit board, make long the life of IC chips, and can be stably used for a long period. The soldering alloy of the present invention is used as foil, thin wire, cream or the like, and also, is applicable to a reflow method in addition to iron soldering and immersion soldering as soldering means. Further, it is possible to use a general rosin-based flux as a flux.

Examples will be described below.

Example 1

Sn, Ag, Bi and Zn of the total weight of 10 kg were weighed so as to have a composition as shown in a Table 1, and then, were melted in graphite crucible with an electric furnace in the air. Next, a melting temperature was set to 300°C, and each metal was fully melted. Thereafter, each metal was sufficiently agitated in order to deprive gravity segregation, and then, was cast in a mold which has an internal dimension of 150 × 60 mm, a height of 150 mm, and a mold thickness of 10 mm. From a lower portion of the resultant casting, a JIS4 test piece was taken out by mechanical process, and then, a tensile strength and a elongation value were measured according to a test method on the basis of a JIS Z2241 test. The results were shown in the following Table 1. Likewise, melted 10 kg metal was cooled as it is, and then, the melting point was obtained from a cooling curve. The results were shown in the following Table 1. Moreover, in order to make a comparison, the same test was made with respect to soldering alloys such as a Pb-Sn eutectic soldering alloy and an alloy H so as to investigate their characteristic, and then, the results were shown in the following Table 1.

Table 1

| | Chemical composition (wt%) | | | | Tensile strength (kgf/mm ²) | Elongation (%) | Melting point (°C) |
|----------------------|----------------------------|-----|----|---------|---|----------------|--------------------|
| | Ag | Zn | Bi | Sn | | | |
| Examples | 3 | 1.5 | 2 | Balance | 4.54 | 31.9 | 213 |
| | 3 | 1.5 | 4 | Balance | 5.46 | 24.2 | 211 |
| | 3 | 1.5 | 6 | Balance | 6.39 | 16.4 | 208 |
| | 3 | 0.5 | 4 | Balance | 5.21 | 26.3 | 214 |
| Comparative examples | 3 | 0 | 4 | Balance | 5.08 | 27.4 | 217 |
| | 3 | 3 | 4 | Balance | 5.83 | 21.2 | 210 |
| | 3 | 1.5 | 1 | Balance | 4.09 | 35.7 | 217 |
| | 3 | 1.5 | 7 | Balance | 6.86 | 12.5 | 207 |
| | Sn-2Ag-0.5Cu-7.5Bi | | | | 6.91 | 12 | 212 |
| | Sn-37Pb | | | | 3.82 | 30 | 183 |

Example 2

Wettability was measured using a Sn-3Ag-1Zn-3Bi alloy as the alloy of the present invention and an alloy H (Sn-2Ag-7.5Bi-0.5Cu) as a comparative example. The wettability test was made under the following conditions. More specifically, zero cross time according to a meniscographic method, that is, a test piece was immersed in a solder bath, and then, values of time and wettability until a buoyant force becomes zero were measured. The results were shown in the following Table 2.

Conditions;

Solder bath temperature: 260°C

Flux: rosin-based flux

Test piece: 0.9 mm Ø × 60 mm Cu wire

Immersed time: 10 seconds
 Immersion velocity: 2 mm/s
 Immersion depth: 2 mm
 Tester: solder checker SAT-2000 type (manufactured of Leska)

Table 2

| | Zero cross time (s) | Wettability (gf) |
|--------------------|---------------------|------------------|
| Sn-3Ag-1Zn-3Bi | 1.48 | 0.0840 |
| Sn-2Ag-7.5Bi-0.5Cu | 1.08 | 0.0940 |

Example 3

Further, in order to investigate an influence of a containing amount of Zn upon wettability, wettability was measured by adding each of Zn:0.5, 1, 2, 3 and 4% by weight to a Sn-3Ag-3Bi alloy. The results were shown in the following Table 3.

Table 3

| Containing amount of Zn (wt%) | 0.5 | 1 | 2 | 3 | 4 |
|-------------------------------|-------|-------|-------|-------|-------|
| Wetting tension (gf) | 0.081 | 0.084 | 0.071 | 0.051 | 0.033 |

Example 4

In order to judge heat fatigue characteristic, a general accelerating test was made with respect to the same soldering alloy of the present invention and alloy H as used in the above Example 2. More specifically, these alloys were kept at a high temperature (150°C) for a predetermined time (0, 100 hours, 300 hours), and thereafter, the tensile strength and elongation were measured. The results were shown in the following Table 4.

Table 4

| | Tensile strength (kgf/mm ²) | | | Elongation (%) | | |
|--------------------|---|-------|-------|----------------|-------|-------|
| | 0hr | 100hr | 300hr | 0hr | 100hr | 300hr |
| Sn-3Ag-1Zn-3Bi | 4.88 | 5.11 | 4.86 | 26.5 | 23.2 | 22.1 |
| Sn-2Ag-7.5Bi-0.5Cu | 6.91 | 5.14 | 5.21 | 12.0 | 4.21 | 4.95 |

As is seen from the Examples, the soldering alloy of the present invention has a low melting point which is almost the same as the alloy H, and is excellent in tensile strength and elongation. Further, in the soldering alloy of the present invention, zero cross time is slightly larger than the alloy H; however, no problem is caused in practical use if zero cross time ranges within 2 seconds. Therefore, the soldering alloy of the present invention is applicable to soldering work. An alloy containing Zn of 3% by weight has wetting tension remarkably lower than an alloy containing Zn of 0.5% by weight. Further, in the soldering alloy of the present invention, both tensile strength and elongation are not so lowered after the soldering alloy is kept at a high temperature. Thus, in the case where the soldering alloy is used in soldering of electronic circuits or the like, heat fatigue characteristic due to a heat from circuits is stable, and it is possible to prevent the breakdown of circuits resulting from deterioration of tensile strength and elongation for a long period, and to improve reliability of soldering portion of circuits or the like.

As described above, according to the present invention, there can be obtained a soldering alloy which has a low melting point equal to the conventional alloy H without containing lead causing environmental contamination, and is excellent in mechanical characteristic, that is, tensile strength and elongation value as compared with the alloy H. Further, there can be a soldering alloy which is excellent in heat fatigue characteristic. Thus, even in the case where temperature cycle is applied, it is possible to absorb a thermal expansion difference between IC substrates and components, and to restrict a risk of damaging products.

Claims

1. A lead-free tin-silver-based soldering alloy consisting essentially of Ag: 2 to 4% by weight, Zn: 0.5 to 2% by weight,

EP 0 882 544 A1

Bi: 2 to 6% by weight, and a balance being substantially Sn.

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EUROPEAN SEARCH REPORT

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EP 98 30 4068

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X | EP 0 612 578 A (AT & T CORP) 31 August 1994 * column 3, line 13 - line 25; claim 1 * | 1 | B23K35/26 C22C13/02 |
| X | EP 0 499 452 A (LANCASHIRE FITTINGS LTD) 19 August 1992 * page 2, line 31 - line 35; table 1 * | 1 | |
| D,A | EP 0 710 521 A (MITSUI MINING & SMELTING CO) 8 May 1996 * abstract * | 1 | |
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| The present search report has been drawn up for all claims | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | B23K C22C |
| Place of search MUNICH | | Date of completion of the search 8 September 1998 | Examiner Pricolo, G |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | |

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